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# Water as a Building Block in Solid-State Acetonitrile–Pyrogallol[4]arene Assemblies: Structural Investigations

**Scott J. Dalgarno, Jochen Antesberger, Robert M. McKinlay, and Jerry L. Atwood***[a]

**Abstract:** Under various conditions, water molecules dramatically affect a number of solid-state *C*-alkylpyrogallol[4]arene assemblies. In the absence of water, hydrogen-bonded hexameric capsules are formed for the *C*-butyl, pentyl, hexyl, and heptyl pyrogallol[4]arenes. Introduction of water to acetonitrile solutions containing *C*-propyl–*C*-octylpyrogallol[4]arenes resulted in the formation of markedly different bilayer structures and the structural identification of two new dimer-type motifs.

**Keywords:** calixarenes • host–guest systems • nanocapsules • pyrogallolarenes • self-assembly

The design and development of novel capsule based systems from small molecular building blocks is an important goal in supramolecular chemistry. Non-covalent capsular systems represent versatile host arrangements that enclose space to varied extents depending on the building blocks employed in structure formation.[1] Calixarenes, or other related bowl-shaped molecules, are excellent molecular frameworks for the design of complementary self-assembling units as they can often be functionalized at the "upper rims" with appropriate supramolecular synthons to aid capsule formation.[1,2]

We, amongst others, have been interested in the self-assembly of *C*-alkylresorcin[4]arene capsules for some time.[3–8,10–11] Six *C*-methylresorcin[4]arenes (CMRC, Figure 1) have been shown to assemble with eight structural water molecules into a hexameric capsule arrangement through concerted hydrogen bonding interactions (as identified by X-ray crystallography).[3] The internal volume of the assembly was ≈1,375 Å$^3$, and is amongst the largest capsular assemblies formed through non-covalent interactions. Additionally, the stability of the assembly in the solution phase has been demonstrated under various conditions in a number of studies.[8,9] More recently, Holman and co-workers showed that the structural water molecules could be replaced with alcohols whilst maintaining the rigidity of the assembly.[10]

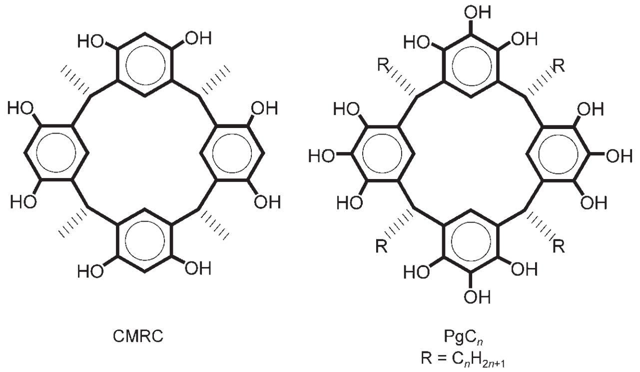

Figure 1. ChemDraw representation showing CMRC and the general PgC$_n$ structure.

The closely related *C*-alkylpyrogallol[4]arenes (PgC$_n$, general structure shown in Figure 1) have been shown to form similar hexameric capsule arrangements in the solid state, also through concerted hydrogen-bonding interactions.[9,12–17] The additional hydroxyl group at the upper rim of the framework precludes the necessity for structural water molecules in the hydrogen-bonded "seam", thereby resulting in increased hexamer stability.[9,12–20] Indeed the stability of these large capsule arrangements has been demonstrated in the solution phase, even when the assemblies are hosting large fluorescent probe molecules.[12] In the presence of water, acetonitrile, and pyrene (or 1-bromopyrene) as a co-crystallizing agent, *C*-hexylpyrogallol[4]arene forms organic nanotube arrangements that shroud alternating MeCN/H$_2$O

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[a] Dr. S. J. Dalgarno, J. Antesberger, Dr. R. M. McKinlay,
Prof. J. L. Atwood
Department of Chemistry, University of Missouri-Columbia
Columbia, MO 65211 (USA)
Fax: (+1) 573-882-2754
E-mail: AtwoodJ@missouri.edu

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Figure of the PgC$_5$ and PgC$_7$ hexameric nanocapsule partial structures.

microenvironments.[21] Given this, we sought to explore the effect water molecules have on the solid-state assembly of a number of *C*-alkylpyrogallol[4]arenes in MeCN, in the absence of other guest molecules. This was examined by crystallizing the selected host molecules from HPLC grade MeCN under various other conditions and performing structural authentication on resulting single crystals. Herein we show that water molecules, present due to atmospheric moisture, or by direct addition, dramatically affect the solid-state assembly of *C*-alkylpyrogallol[4]arenes. Studies by Rebek and co-workers showed the formation and structural characterization of a $PgC_3$ hydrogen-bonded dimer from 20% aqueous acetonitrile (type I dimer).[7] By studying $PgC_3$–$PgC_8$ under the aforementioned conditions, we have structurally characterized two hydrogen-bonded hexamers (for $PgC_4$ and $PgC_6$), and three new bilayer motifs, two of which form as dimeric capsule arrangements that differ from the type I arrangement reported by Rebek.[7] In addition, we have partially characterized two other hexamers (from $PgC_5$ and $PgC_7$) although these produced small weakly diffracting crystals which at best only allowed for the identification of the majority of the Pg frameworks (unit cells for these hexamers are included in the Experimental Section).

## Results and Discussion

Each of the six pyrogallol[4]arene monomers were dissolved in boiling HPLC grade acetonitrile and then allowed to crystallize by different methods; 1) direct capping of the crystallizing vessel; 2) cooling and evaporation in the presence of atmospheric moisture; 3) cooling and evaporation after the addition of one equivalent of water (by volume). For all but $PgC_3$ and $PgC_8$, method 1 resulted in the growth of single crystals containing the corresponding hydrogen-bonded hexamers. For $PgC_3$, an alternative bilayer arrangement formed through the incorporation of one water molecule per pyrogallol[4]arene. Method 2 was typically unsuccessful in the formation of single crystals although a dimeric capsule arrangement was formed for $PgC_6$ (new type II bilayer). Method 3 produced three different structural motifs for $PgC_3$–$PgC_8$. The type I Rebek bilayer dimer was formed for $PgC_3$, whilst all the remaining pyrogallol[4]arenes except $PgC_6$ formed type II bilayer dimers. For $PgC_6$, an expanded bilayer dimer formed that included a ring of water molecules around the upper rims of the pyrogallol[4]arenes (new type III dimer).

***C*-Propylpyrogallol[4]arene**: As mentioned in the Introduction, Rebek and co-workers crystallized $PgC_3$ from an aqueous acetonitrile solution to afford a type I dimeric capsule arrangement in the solid state (Figure 2a).[7] In that study, the authors found $PgC_3$ to be insoluble in acetonitrile without the presence of 20% of water by volume (similar to method 3 outlined above). In slight contrast to this, we found that by continuously boiling $PgC_3$ in HPLC grade MeCN, dissolution of the compound could be achieved. The vessel was stoppered, cooled, and left to sit over several weeks with a lack of single crystal growth (method 1). Concomitant slow evaporation in the presence of atmospheric moisture (method 2) resulted in the growth of colorless single crystals that were suitable for X-ray diffraction studies (**1**, Table 1). The asymmetric unit in **1** was found to comprise one $PgC_3$, two molecules of MeCN (that are disordered over five positions) and one water of crystallization (Figure 2b). Symmetry expansion of the asymmetric unit resulted in the formation of a bilayer structure (Figure 2c) that is stabilized by a large number of hydrogen-bonding interactions (some of which are shown in Figure 2d). One of the disordered MeCN molecules resides in the $PgC_3$ cavity, and in each of the three disordered positions, shows $CH\cdots\pi$ interactions between the methyl group and Pg aromatic rings (CH···aromatic centroids distances ranging from 2.575 to 2.874 Å). The water of crystallization takes part in the hydrogen-bonding regime with "upper rim" hydroxyl groups; the $H_2O$ acts as both an acceptor (ArOH···O distance of 1.858 Å) and a donor (two OH···HOAr distances of 2.088 and 2.229 Å, Figure 2d).

The use of method 3 for crystallization resulted in the formation of the type I dimer (confirmed by comparing single crystal unit cell dimensions, see Experimental Section),[7] and although relatively dry solvent techniques were employed in method 1 for $PgC_3$, the growth of single crystals of the corresponding hexamer did not occur.

***C*-Butylpyrogallol[4]arene**: For $PgC_4$, methods 1 and 3 were successful in the growth of single crystals that were suitable for X-ray diffraction studies. When method 1 was employed, large colorless single crystals grew in the sealed sample vial. The crystals were of trigonal symmetry and upon structural solution, the asymmetric unit was found to contain one $PgC_4$ and a total of 1.75 MeCN molecules that were identifiable in the electron density map (**2**, Table 1). Three quarters of the $PgC_4$ molecule showed disorder, as did the solvent molecules which were disordered over several positions. Despite this, the quality of the data allowed for satisfactory modeling of the disorder and elucidation of the structure as a hexameric $PgC_4$ nanocapsule (Figure 3). As is the case for other hydrogen-bonded $PgC_n$ nanocapsules, **2** is stabilized by similar non-covalent interactions at the nanocapsule "seam", the distances of which are all in agreement with previously reported structural analyses.[12,13,17]

Although method 2 did not afford suitable single crystals, method 3 was successful and structural authentication revealed a bilayer structure similar to that described for $PgC_3$. Structure refinement was problematic and resulted in a very high $R_1$ factor. Given this, only the unit cell dimensions for this structure have been included in the Experimental Section. It should be noted, however, in the context of this contribution, that the $PgC_4$ molecules in the extended structure of the bilayer do not assemble in dimeric or hexameric capsule-like fashions.

Table 1. X-ray data for crystal structures **1**–**8**.

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| empirical formula | $C_{44}H_{56}N_2O_{13}$ | $C_{48}H_{62}N_2O_{12}$ | $C_{50}H_{69}N_1O_{13}$ | $C_{130}H_{183}N_{13}O_{24}$ |
| molecular mass | 820.91 | 859.01 | 892.06 | 2311.89 |
| crystal size [mm] | 0.6 × 0.55 × 0.48 | 0.2 × 0.2 × 0.16 | 0.3 × 0.2 × 0.2 | 0.4 × 0.36 × 0.35 |
| crystal system | monoclinic | trigonal | monoclinic | triclinic |
| space group | $P2_1/c$ | $R\bar{3}$ | $P2_1/c$ | $P\bar{1}$ |
| $T$ [K] | 173(2) | 173(2) | 173(2) | 173(2) |
| $a$ [Å] | 19.668(4) | 35.890(3) | 19.115(3) | 19.573(3) |
| $b$ [Å] | 11.479(3) | | 13.237(2) | 22.624(4) |
| $c$ [Å] | 20.140(4) | 21.458(4) | 19.685(3) | 23.425(4) |
| $\alpha$ [°] | 90 | 90 | 90 | 69.761(3) |
| $\beta$ [°] | 104.404(3) | 90 | 90.668(3) | 69.973(3) |
| $\gamma$ [°] | 90 | 120 | 90 | 71.867(3) |
| $V$ [Å3] | 4404.1(17) | 23937(5) | 4980.4(15) | 8922(3) |
| $Z$ | 4 | 24 | 4 | 2 |
| $\rho_{calcd}$ [$Mg\,m^{-3}$] | 1.238 | 1.43 | 1.19 | 0.861 |
| $\theta$ range [°] | 2.07, 27.13 | 1.62, 27.11 | 1.85, 27.14 | 1.55, 27.17 |
| reflections collected | 30565 | 13752 | 42557 | 63870 |
| independent reflections ($R$int) | 9690 (0.0209) | 10757 (0.0355) | 10983 (0.0435) | 38394(0.0287) |
| parameters | 608 | 570 | 675 | 1772 |
| final $R1$ [$I > 2\sigma(I)$] | 0.0453 | 0.1524 | 0.0512 | 0.1532 |
| $S$ | 1.025 | 1.563 | 1.023 | 2.017 |
| $wR2$ (all data) | 0.13 | 0.378 | 0.1651 | 0.411 |
| min, max residual electron density [$e\,Å^3$] | −0.364, 0.689 | −0.67, 1.204 | −0.307, 0.706 | −0.516, 1.534 |

| | **5** | **6** | **7** | **8** |
|---|---|---|---|---|
| empirical formula | $C_{55}H_{76.50}N_{1.50}O_{13}$ | $C_{54}H_{91}NO_{20}$ | $C_{54.50}H_{85.75}N_{1.25}O_{13}$ | $C_{62}H_{93}NO_{13}$ |
| molecular mass | 966.68 | 1074.28 | 966.49 | 1060.37 |
| crystal size [mm] | 0.37 × 0.32 × 0.26 | 0.6 × 0.3 × 0.3 | 0.45 × 0.26 × 0.2 | 0.36 × 0.23 × 0.18 |
| crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ |
| $T$ [K] | 173(2) | 173(2) | 173(2) | 173(2) |
| $a$ [Å] | 20.239(2) | 10.643(3) | 21.296(4) | 22.702(5) |
| $b$ [Å] | 13.3106(15) | 12.307(3) | 13.449(3) | 13.455(3) |
| $c$ [Å] | 19.726(2) | 23.180(6) | 19.813(4) | 19.717(4) |
| $\alpha$ [°] | 90 | 94.457(4) | 90 | 90 |
| $\beta$ [°] | 90.101(2) | 100.680(4) | 90.260(4) | 93.174(7) |
| $\gamma$ [°] | 90 | 97.126(4) | 90 | 90 |
| $V$ [Å3] | 5313.9(10) | 2944.8(14) | 5674.5(19) | 6013(2) |
| $Z$ | 4 | 2 | 4 | 4 |
| $\rho_{calcd}$ [$Mg\,m^{-3}$] | 1.208 | 1.212 | 1.131 | 1.171 |
| $\theta$ range [°] | 1.83, 27.13 | 1.68, 27.14 | 1.79, 27.18 | 1.76, 27.2 |
| reflections collected | 29521 | 25576 | 34490 | 28519 |
| independent reflections ($R$int) | 11323 (0.0375) | 12760 (0.0232) | 12462 (0.0368) | 12888 (0.1026) |
| parameters | 732 | 1016 | 837 | 713 |
| final $R1$ [$I > 2\sigma(I)$] | 0.0592 | 0.0524 | 0.0559 | 0.0998 |
| $S$ | 1.019 | 1.031 | 1.02 | 1.074 |
| $wR2$ (all data) | 0.1645 | 0.1471 | 0.1484 | 0.2599 |
| min, max residual electron density [$e\,Å^3$] | −0.378, 0.631 | −0.251, 0.532 | −0.306, 0.478 | −0.769, 1.247 |

***C*-pentylpyrogallol[4]arene**: As for $PgC_4$, methods 1 and 3 were successful for single crystal growth while method 2 was not. The crystals grown by method 1 were colorless, of triclinic symmetry and were weakly diffracting. As the X-ray data was of limited quality, it was only possible to observe the gross connectivities between the majority of the $PgC_5$ framework atoms in the structural solution (shown in Supporting Information). Although checking for additional symmetry shows that the correct space group is $P\bar{1}$, a reasonable structural solution could only be achieved in $P1$. In the former, two half $PgC_5$ hexamers were superimposed upon one another in the structural solution. Solution in the latter space group revealed an entire $PgC_5$ hexamer without superimposition. Numerous data collections on different sized crystals could not resolve the problem of data weakness.

The crystals grown by method 3 were of monoclinic symmetry and upon structural solution, the asymmetric unit was found to contain one $PgC_5$, one MeCN molecule and one water of crystallization (**3**, Table 1). The MeCN was found to reside in the $PgC_5$ cavity and interact via CH···π interactions (two CH···aromatic centroid distances of 2.657 and 2.746 Å). Symmetry expansion around the acetonitrile guest molecule resulted in the formation of a new dimeric capsule arrangement in which there are cooperative intermolecular interactions between all the molecular components to stitch the capsule together (Figure 4a). These are in the form of three crystallographically unique hydrogen-bonding interactions, all of which are shown in Figure 4a: one ArOH···NCMe interaction with an OH···N distance of 1.877 Å; one ArOH···O($H_2O$) interaction with an OH···O distance of 1.779 Å; one ($H_2O$)OH···OAr interaction with an OH···O distance of 1.895 Å. When examining the further role that water plays in this assembly of $PgC_5$, it is found to accept an additional hydrogen bond from another $PgC_5$ "upper rim" hydroxyl group (ArOH···O($H_2O$) distance of 1.910 Å), and to hydrogen-bond to another neighboring $PgC_5$ "upper rim" hydroxyl group (($H_2O$)OH···OAr distance of 1.878 Å) as shown in Figure 4b.

***C*-hexylpyrogallol[4]arene**: Single crystals were grown for $PgC_6$ under all three crystallization conditions. Method 1 afforded large colorless single crystals that were of triclinic symmetry (**4**, Table 1). Structural solution showed the asymmetric unit to contain three $PgC_6$ molecules and several badly disordered MeCN molecules. Symmetry expansion re-

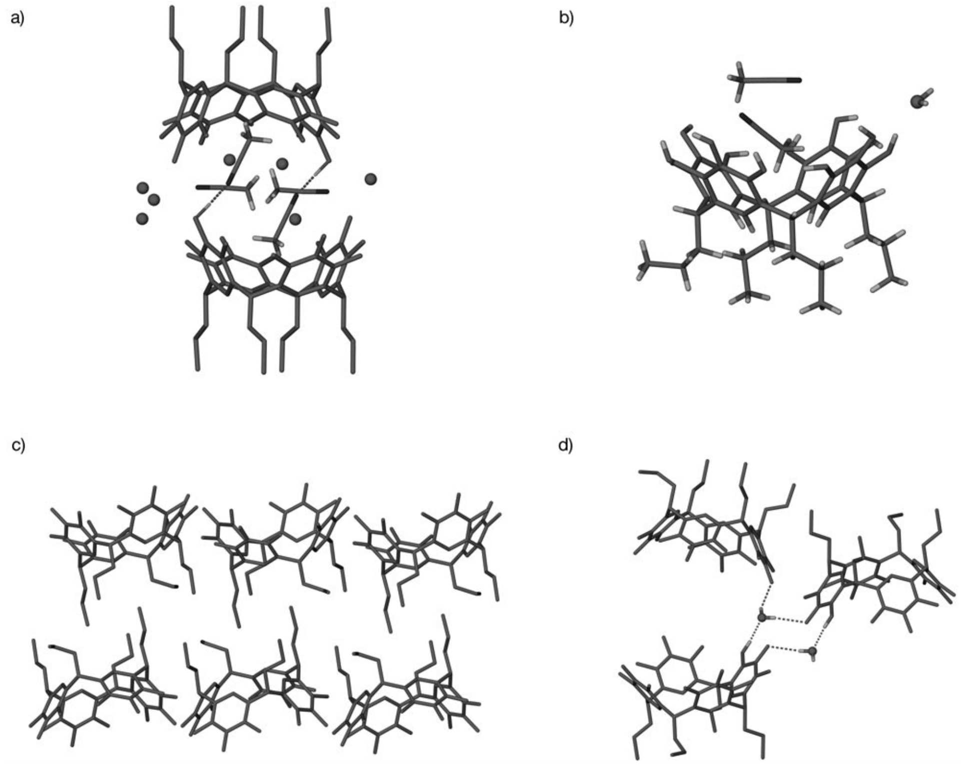

Figure 2. Diagrams showing a) the Type I dimer,[7] b) the asymmetric unit in **1**, c) part of the extended bilayer structure in **1**, and d) hydrogen-bonding interactions associated with the water of crystallization in **1**. Hydrogen atoms and solvent molecules have been omitted for clarity in most instances (except for b, and cases in which specific interactions or guest presence is shown). Figure are not to scale. In b)–d), disordered groups or solvent molecules are only shown in one position. Hydrogen bonds are shown as dashed lines.

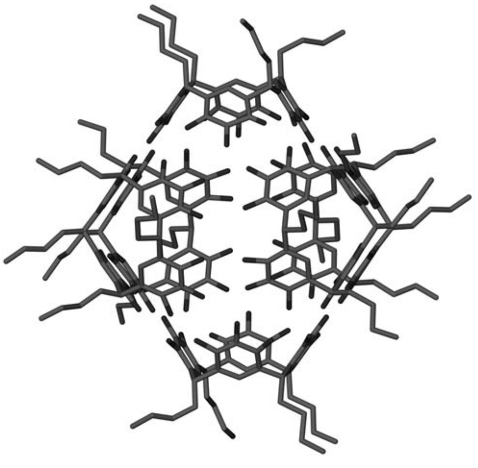

Figure 3. Hydrogen-bonded $PgC_4$ hexameric nanocapsule **2** formed by crystallization method 1. Hydrogen atoms and solvent molecules have been omitted for clarity. The disordered $PgC_4$'s are only shown in one position.

vealed the extended structure to be based on the hexameric nanocapsule motif (Figure 5a) similar to that for $PgC_4$. When crystals of $PgC_6$ nanocapsules are grown from ethyl acetate, the hydrogen-bonded seam is disrupted and neighboring capsules hydrogen-bond to one another from "upper rim" hydroxyl groups.[13] This is not the case in **4**; the hydrogen-bonded "seam" is entirely intra-molecular (with respect to the hexamer) and all OH···O distances are of typical magnitude to those observed in **2**, and other reported hexamers that were crystallized from MeCN.[12,17]

Crystallization of $PgC_6$ via method 2 resulted in the growth of large colorless single crystals that were of monoclinic symmetry (**5**, Table 1). Structure solution showed the asymmetric unit to contain one $PgC_6$, 1.5 MeCN molecules and one water of crystallization. Symmetry expansion revealed a type II dimer that is very similar to that found in **3**. The full occupancy MeCN molecule occupies the $PgC_6$ cavity and forms CH···π interactions with CH···aromatic centroids distances of 2.629 and 2.719 Å. The dimeric capsule is stitched together by an essentially identical hydrogen-bonding regime as shown in Figure 5b: one ArOH···NCMe interaction with an OH···N distance of 1.870 Å; one ArOH···O($H_2O$) interaction with an OH···O distance of 1.842 Å; one ($H_2O$)OH···OAr interaction with an OH···O distance of 1.790 Å. Indeed the extended structure differs only slightly due to the presence of a half-occupancy *exo*-cavity MeCN molecule.

Crystallization of $PgC_6$ via method 3 resulted in the growth of large colorless single crystals that were of triclinic symmetry (**6**, Table 1). Surprisingly, the asymmetric unit was found to contain one $PgC_6$, one MeCN molecule and eight waters of crystallization (Figure 6a). This was unexpected given that crystals of **3** were grown under identical conditions, and that only one water of crystallization was found in the asymmetric unit. In a similar way to structures **3** and **5**, the MeCN molecule occupies the Pg cavity and forms CH···π interactions with CH···aromatic centroids distances of 2.514 and 2.581 Å. Symmetry expansion around the MeCN guest reveals a dimeric capsule arrangement that appears to have been expanded (relative to structure **5**) by the inclusion of the eight waters of crystallization (Figure 6b). Indeed, the distance between centroids generated at the lower $PgC_6$ rims in the dimeric capsules **5** and **6**, shows an approximate increase in capsule length from 9.4 to 11.3 Å, respectively. The hydrogen-bonding regime in and around the capsule interior or seam is complicated and the general dimer motif is maintained by these numerous concerted in-

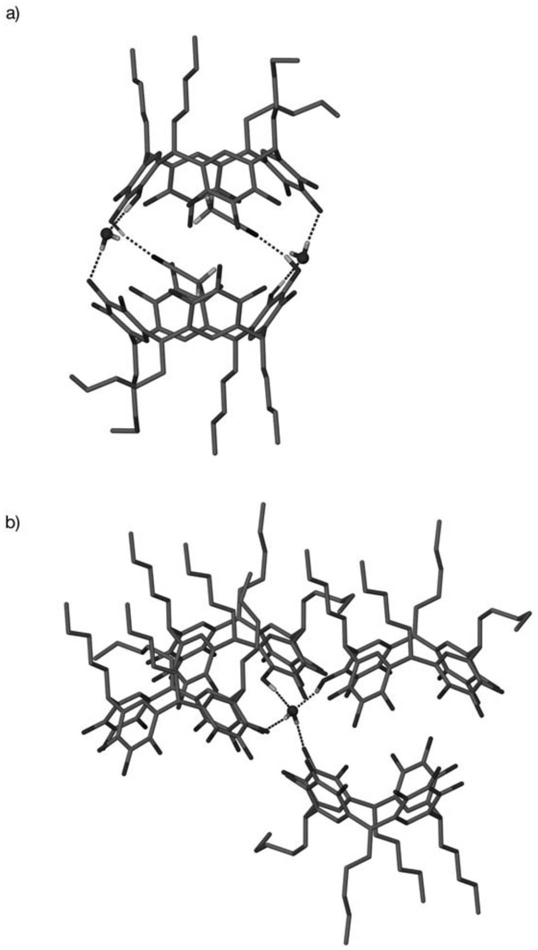

Figure 4. Diagrams of a) the type II dimer **3** formed from PgC$_5$ under crystallization method 3, and b) part of the extended structure of **3** showing hydrogen-bonding interactions associated with the water of crystallization. Hydrogen atoms (except those shown for guest molecules and specific interactions) are omitted for clarity. Hydrogen bonds are shown as dashed lines.

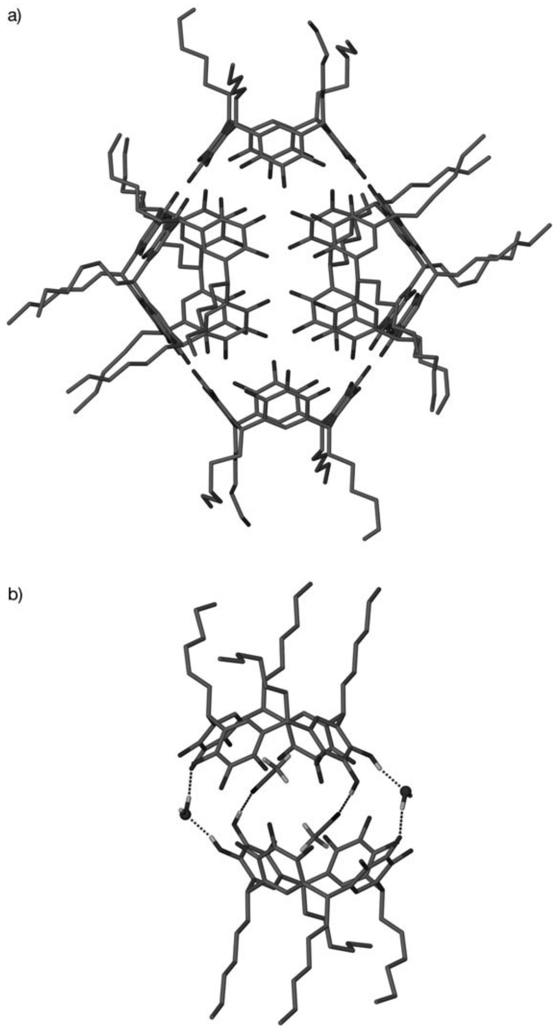

Figure 5. Crystal structures of a) the PgC$_6$ hexameric nanocapsule **4**, and b) the type II dimer **5** formed from PgC$_6$ by method 2. Hydrogen atoms (except those shown for guest molecules and specific interactions) are omitted for clarity. Hydrogen bonds are shown as dashed lines. Figure not to scale.

teractions (some of which are shown in Figure 6c). Further symmetry expansion reveals a very complicated hydrogen-bonding regime between the upper rim PgC$_6$ hydroxyl groups and the waters of crystallization (partly shown in Figure 6d).

Notably, it is possible to synthesize organic nanotubes in the solid state by crystallizing PgC$_6$ under similar conditions to those used in method 3, but also with a co-crystallizing agent (pyrene or 1-bromopyrene).[21] The fact that PgC$_6$ is the only member of this family of molecules to display such behavior to date may relate to the type III dimer reported here, and the affinity of the host to crystallize with a large number of water molecules.

***C*-heptylpyrogallol[4]arene**: For PgC$_7$, the results of the three crystallization methods were essentially the same as for PgC$_5$. Method 1 produced small colorless crystals that were weakly diffracting. The crystals were of triclinic symmetry and data collection revealed the structure to be a hexameric nanocapsule. Due to the weakness of the data, as was the case for PgC$_5$, it was only possible to observe the gross connectivities between the majority of the hexamer framework atoms (shown in Supporting Information).

Although method 2 was unsuccessful in single crystal growth, method 3 produced colorless single crystals that were suitable for diffraction studies (**7**, Table 1). The crystals were of monoclinic symmetry and upon structural solution, the asymmetric unit was found to contain one PgC$_7$, 1.25 MeCN molecules and one water of crystallization. The full occupancy MeCN resides in the PgC$_7$ cavity and forms two CH···π interactions with CH···aromatic centroid distances of 2.597 and 2.780 Å. Symmetry expansion around the MeCN guest shows the structure to be a type II dimer similar to **3** and **5** (Figure 7). The dimeric capsule is stitched together by a similar hydrogen-bonding regime to that shown in Fig-

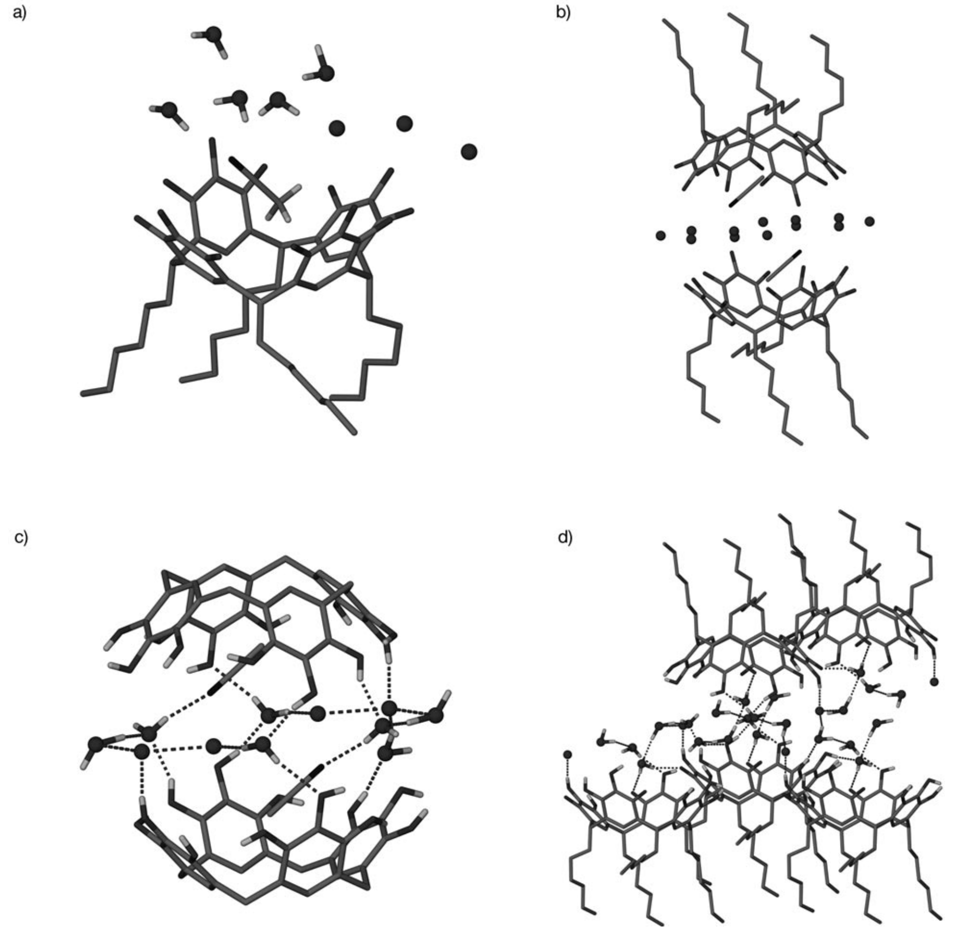

Figure 6. Diagrams of the crystal structure of the type III dimer **6** showing a) the asymmetric unit, b) the expanded dimeric capsule arrangement, c) part of the extensive hydrogen-bonding regime in and around the dimer ($PgC_6$ *C*-hexyl chains removed for clarity), and d) hydrogen-bonding interactions found in part of the extended structure. Hydrogen atoms (except those shown for guest molecules and specific interactions) are omitted for clarity. Hydrogen bonds are shown as dashed lines. Figure not to scale.

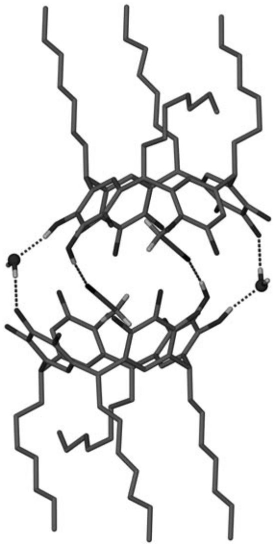

Figure 7. Type II dimer **7** formed from $PgC_7$ under crystallization method 3. Hydrogen atoms (except those shown for guest molecules and specific interactions) are omitted for clarity. Hydrogen bonds are shown as dashed lines.

ure 5b: one ArOH···NCMe interaction with an OH···N distance of 1.887 Å; one ArOH···O($H_2O$) interaction with an OH···O distance of 1.861 Å; one ($H_2O$)OH···OAr interaction with an OH···O distance of 1.909 Å.The extended structure is also similar to that described for **3** with respect to the hydrogen-bonding between the water of crystallization and neighboring $PgC_7$ molecules.

***C*-octylpyrogallol[4]arene**: For $PgC_8$, only method 3 was successful in the growth of suitable single crystals. Whilst method 2 was completely unsuccessful, method 1 did produce very small colorless single crystals that were very weakly diffracting and unsuitable for diffraction studies.

By employing method 3, large colorless single crystals of monoclinic symmetry were grown (**8**, Table 1). Upon structural solution, the asymmetric unit was found to contain one $PgC_8$, one MeCN molecule and one water of crystallization. As for **3**, **5** and **7**, the MeCN was found to form CH···π interactions with the $PgC_8$ (CH···aromatic centroid distances of 2.628 and 2.753 Å). Symmetry expansion around the MeCN guest showed the structure to be a type II dimer similar to **3**, **5**, and **7** (Figure 8). This type II dimer is also stitched together by similar hydrogen-bonding interactions to those shown in Figure 5b: one ArOH···NCMe interaction with an OH···N distance of 1.914 Å; one ArOH···O($H_2O$) interaction with an OH···O distance of 1.871 Å; one ($H_2O$)OH···OAr interaction with an OH···O distance of 1.920 Å. The extended structure was also found to be similar with respect to hydrogen bonding from the water of crystallization to neighboring $PgC_8$ molecules.

## Conclusion

**Method 1**: For $PgC_3$–$PgC_8$, relatively dry conditions in acetonitrile generally resulted in the formation of hydrogen-bonded hexamers in the solid state ($PgC_4$ and $PgC_6$, although for $PgC_5$ and $PgC_7$ this is based on a partial structure solution that shows the general hexamer motif).

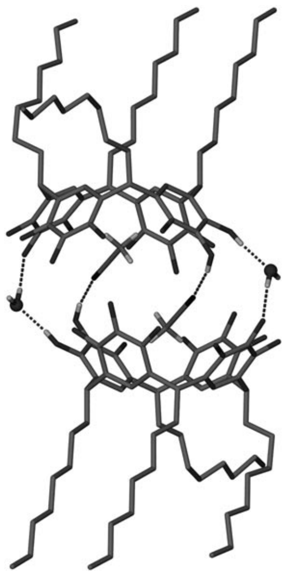

Figure 8. Type II dimer **8** formed from $PgC_8$ under crystallization method 3. Hydrogen atoms (except those shown for guest molecules and specific interactions) are omitted for clarity. Hydrogen bonds are shown as dashed lines.

**Method 2**: Evaporation of $PgC_n$ acetonitrile solutions did not result in the growth of single crystals except for the $PgC_6$ case in which a new type II dimer formed.

**Method 3**: For $PgC_{5,7,8}$, addition of one equivalent (by volume) of water to the crystallization solution resulted in the formation of type II dimers. For $PgC_3$, these conditions resulted in the formation of the type I dimer, while for $PgC_4$, it was not possible to grow single crystals that were more suitable for diffraction studies. For $PgC_6$, this set of conditions resulted in the formation of a new expanded bilayer dimer (type III) which shows some similarities to the type I dimer.

In summation, water molecules can dramatically alter the way pyrogallol[4]arenes assemble in the solid state (Table 2). The type II dimer is somewhat general for those PgCs examined here, but particular "lower rim" chain length appears to play an important role in determining the self-assembly on occasion, as demonstrated by the crystallization of $PgC_6$ via method 3. Having insight into the assembly of PgCs with $H_2O$ may prove useful in engineering other nanoscale arrays based on these useful host molecules. Notably, we have to date only found alternative tubular structures for $PgC_6$ (when co-crystallized with pyrene or 1-bromopyrene), structures that incorporate large amounts of both acetonitrile and water.[20] Perhaps the fact that $PgC_6$ behaves so differently in these less complicated bilayer structures is an indicator that $PgC_3$ may exhibit similar behavior under alternative crystallization conditions given the nature of the type I dimer. This is an avenue we are currently exploring, as is the alternative growth of larger single crystals of other pyrogallol[4]arenes hexamers ($PgC_n$, where $n > 7$).

Table 2. Summary of structural types found for $PgC_3$–$PgC_7$ under each crystallization condition (methods 1–3).

| $PgC_n$ | Method 1 (MeCN) | Method 2 (MeCN + moisture) | Method 3 (MeCN + 1 equiv by vol. $H_2O$) |
|---|---|---|---|
| $PgC_3$ | NSC | bilayer | type I dimer |
| $PgC_4$ | hexamer | NSC | bilayer[*] |
| $PgC_5$ | hexamer | NSC | type II dimer |
| $PgC_6$ | hexamer | type II dimer | type III dimer |
| $PgC_7$ | hexamer | NSC | type II dimer |
| $PgC_8$ | UC | NSC | type II dimer |

UC = unsuitable crystals, NSC = no single crystals. [*] The data for this structure is of poor quality and resulted in a very high *R* factor. For this reason, only unit cell parameters for this structure are included in the experimental section.

## Experimental Section

The *C*-alkylpyrogallol[4]arenes were prepared according to literature procedures.[13,17] HPLC grade acetonitrile was purchased from Aldrich and used as supplied. Crystals were grown by one of three different methods.

**Method 1**: Typically around 100 mg of the selected $PgC_n$ was placed in a sample vial and dissolved in the minimum amount of hot HPLC grade MeCN. Once dissolved, the vial was capped and allowed to stand for up to three weeks. Successful crystal growth was typically achieved over a several day period.

**Method 2**: Method 1 was followed as above, but the solution in the vial was allowed to evaporate at room temperature over 1–2 weeks. Upon observation of single crystal growth, the sample vial was capped to preserve the single nature of the crystals.

**Method 3**: Methods 1 and 2 were followed as above, but one equivalent (by volume) of water was added prior to the evaporation step in method 2.

**X-ray crystallography**: CCDC-637093–637100 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***C*-Propylpyrogallol[4]arene**: Unit cell dimensions of the crystals obtained by method 3, matching those of the type I dimer: Triclinic, $a = 11.4831(19)$, $b = 11.6527(19)$, $c = 18.7057(31)$ Å, $\alpha = 77.1831(27)$, $\beta = 89.9186(29)$, $\gamma = 77.1131(30)°$, $V = 2376(1)$ Å$^3$. Unit cell dimensions of the type I dimer: Triclinic, $a = 11.455(1)$, $b = 11.627(1)$, $c = 18.662(2)$ Å, $\alpha = 102.785(2)$, $\beta = 90.042(2)$, $\gamma = 102.881(2)°$, $V = 2360.0(4)$ Å$^3$.[7]

***C*-Butylpyrogallol[4]arene**: Unit cell dimensions for the $PgC_4$ bilayer structure: Triclinic, space group $P\bar{1}$, $a = 13.1171(62)$, $b = 18.0394(83)$, $c = 19.7451(92)$ Å, $\alpha = 82.2086(79)$, $\beta = 82.2086(79)$, $\gamma = 89.3717(82)°$, $V = 4445(6)$ Å$^3$.

***C*-Pentylpyrogallol[4]arene**: Unit cell dimensions for the $PgC_5$ hexamer partial structure: Triclinic, $a = 19.4434(45)$, $b = 22.0224(53)$, $c = 22.6750(53)$ Å, $\alpha = 69.2108(35)$, $\beta = 70.8572(37)$, $\gamma = 71.3756(33)°$, $V = 8346(6)$ Å$^3$. Due to the weakly diffracting nature of these crystals, only the gross connectivities between the majority of the main $PgC_5$ framework atoms could be identified (Supporting Information).

***C*-Heptylpyrogallol[4]arene**: Unit cell dimensions for the $PgC_7$ hexamer: Triclinic, $a = 22.1670(46)$, $b = 22.3823(50)$, $c = 22.3432(47)$ Å, $\alpha = 93.4836(48)$, $\beta = 100.2924(52)$, $\gamma = 118.8329(50)°$, $V = 9415(6)$ Å$^3$. Due to the weakly diffracting nature of these crystals, only the gross connectivities between the majority of the main $PgC_7$ framework atoms could be identified (Supporting Information).

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